ARB Project 5-143-2

ARB Contract No. 023

AIR RESOURCES BOARD
LIBRARY
A Q S

FINAL REPORT

Title of Project: Photochemical Smog: Reactions of Hydroxyl with Aldehydes.

Institution: University of California, Davis

Period Covered: July 1, 1971 through March 31, 1972

Title of Report: Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System: Rate Constants for Hydroxyl Radical Reactions by Competitive Kinetics

Principal Investigator: David H. Volman, Professor of Chemistry

Personnel: David H. Volman, Professor of Chemistry
Robert A. Gorse, Research Assistant

LIBRARY
AIR RESOURCES BOARD
P. O. BOX 2815
SACRAMENTO, CA 95812

PHOTOCHEMISTRY OF THE GASEOUS HYDROGEN PEROXIDE-CARBON MONOXIDE SYSTEM: RATE CONSTANTS FOR HYDROXYL RADICAL REACTIONS BY COMPETITIVE KINETICS

ABSTRACT

The reaction between hydrogen peroxide and carbon monoxide initiated by absorption of 254 nm light at 298°K in a static system has been studied. Hydroxyl radicals were formed in the primary process and reacted with carbon monoxide to yield carbon dioxide and hydrogen atoms. Hydrogen atoms reacted with hydrogen peroxide either to yield H_2O and OH or to yield H_2 and HO_2. For these processes the rate constant ratio was found to be $k_{H_2O}/k_{H_2} = 3.0 \pm 1.0$. With sufficient added oxygen hydrogen atoms reacted only with oxygen to yield HO_2 and it was possible to obtain a rate constant for the reaction of OH with H_2O_2. With both oxygen and isobutane added, it was possible to obtain a rate constant for the reaction of OH with $(CH_3)_3CH$. The constants obtained were $k_{OH+H_2O_2} = 1.2 \pm 0.3 \times 10^{-12}$ and $k_{OH+(CH_3)_3CH} = 3.5 \pm 0.8 \times 10^{-12}$ cm^{3}molecule^{-1}sec^{-1}. Preliminary results for the reaction with propionaldehyde were also obtained yielding the tentative rate constant $k_{OH+(C_2H_5)CHO} = 3.8 \pm 1.5 \times 10^{-12}$ cm^{3}molecule^{-1}sec^{-1}.

INTRODUCTION

The reactions of hydroxyl free radical are of considerable interest both inherently and because they play an important role in combustion, flames, explosions, and reactions in planetary atmospheres. The reaction with carbon monoxide yielding carbon dioxide and hydrogen atoms has attracted special attention recently because it appears to be involved in contaminated atmospheres, perhaps contributing by subsequent reactions to ozone formation in photochemical smog in the lower atmosphere and to ozone depletion in the upper atmosphere. Further, an understanding of the reaction of hydroxyl with other contaminants in polluted atmospheres is important for the development of models of photochemical smog.

A primary objective of this work was to obtain rate constants for the reaction of hydroxyl with aldehydes. Because of time limitations and complexities introduced by the aldehydes we were not able to satisfactorily obtain this objective. It should be emphasized, however, that we have developed a method of obtaining rate constants for hydroxyl radical reactions and have applied it to hydrogen peroxide and isobutane, compounds of interest in the photochemistry of polluted atmospheres.

The photochemical decomposition of gaseous hydrogen peroxide at 254 nm has been explained by assuming a single primary process, the formation of $OH(^2\Pi)$.[1,2] This reaction may therefore be used as a source of hydroxyl radicals for kinetic studies. It seemed to us that in a mixture of hydrogen peroxide, carbon monoxide, and an added gas with which hydroxyl could react, it would be possible to obtain rate constants by a method of competitive reactions based solely on the determination of carbon dioxide formation. This proved to be the case provided oxygen

was also added to the system. In the present paper we report results and conclusions from the following systems: hydrogen peroxide; hydrogen peroxide-carbon monoxide; hydrogen peroxide-carbon monoxide-oxygen; and hydrogen peroxide-carbon monoxide-oxygen-isobutane. In addition preliminary results with an aldehyde, propionaldehyde, are reported.

EXPERIMENTAL

Materials

Hydrogen peroxide, FMC Corporation 90% aqueous, was distilled under vacuum at 0°C to yield about a 95% solution which was stored at dry-ice temperature prior to use. The isobutane was 99.9% purity Phillips Research Grade with the only impurity detectable being n-butane. Propionaldehyde, Eastman Kodak Company, was purified by vacuum distillation at -78°C. No impurities were found by mass spectrometry. ^{18}O labelled oxygen obtained from ICN corporation was 93.5 atom percent ^{18}O as determined by mass spectrometry. Carbon monoxide and oxygen, high-purity gases in cylinders, were collected after passage through a bath at liquid-nitrogen temperature. Mass spectrometry indicated traces of carbon dioxide in the carbon monoxide and nitrogen in the oxygen.

Apparatus

The experimental arrangement was analogous to that used previously.[1] The reaction cell was a quartz-jacketed cylindrical-quartz vessel, 2.5x25.0 cm, in which constant temperature was maintained by circulating thermostated water through the outer jacket. The light source was a dc-operated helical mercury resonance arc housed in Vycor to limit the

effective transmitted light to 254 nm. Pressure was monitored by a spoon-type Bourdon gauge amplified by an optical-lever system employing a laser beam reflected from a silver mirror mounted on the tip of the gauge. A null method was used in conjunction with a dibutylphthalate manometer to obtain absolute pressures. The analysis system consisted of a series of three Volman traps,[3] an automatic Toepler pump, a gas burette, a switching line to an on-line VPC, and connections to mass spectrometer sample tubes.

Procedures

Hydrogen peroxide was introduced into the evacuated reaction cell by allowing the cell to come to equilibrium with the hydrogen peroxide solution maintained in a bath at about 18°C. Other gases were introduced from storage vessels by expansion from an inlet system. The reactants were allowed to mix for 15 minutes prior to irradiation which was initiated by removing a cylindrical shutter surrounding the reaction vessel.

After irradiation the reaction mixture was drawn through the trap system by the automatic-Toepler pump. The first trap was held at 77°K until all non-condensable gases were pumped into the gas burette. The reaction cell was closed to the pumping system and the first trap was allowed to warm to ambient temperature while the second and third traps were maintained at -78°C. Finally, the second trap was warmed to ambient temperature. The total volume of gas collected was determined in the gas burette, and samples were taken for mass spectrometer and VPC analysis. The two methods gave the same result within experimental error but mass spectrometry was the predominant means of analysis employed.

Because a mercury resonance arc was the light source, it was essential to exclude mercury from the reaction vessel to avoid photosensitization. The absence of mercury from the cell was periodically checked by irradiating a mixture of carbon monoxide and oxygen. Carbon dioxide was never formed in these experiments.

RESULTS

Hydrogen peroxide

In earlier work[1] it was found that the photodecomposition of hydrogen peroxide at 254 nm was not affected by added nitrogen, oxygen, or water. In the present work preliminary experiments showed that the same results were obtained with either hydrogen peroxide alone or with added carbon dioxide. Therefore, to eliminate the possibility of wall effects and to approximate subsequent conditions, 16.0 Torr of carbon dioxide was used. The initial peroxide pressure was 0.94 Torr as determined by measuring the oxygen yield obtained on complete photolysis of peroxide. Experiments were carried out at three different intensities corresponding to arc currents of 1.0, 8.0, and 15.0 milliampers. The results obtained, plotted in accordance with the known mechanism of hydrogen peroxide photolysis[1,2] and later discussion, are shown in Fig. 1. Each point represents a separate experiment starting with a fresh sample of hydrogen peroxide.

Hydrogen peroxide-carbon monoxide

Mixtures of hydrogen peroxide and carbon monoxide were irradiated and the yields of products were determined, Fig. 2. Each point is the result of a separate experiment with the same initial conditions: arc, 8.0 ma; hydrogen peroxide, 0.94 Torr; carbon monoxide, 16.2 Torr.

Hydrogen peroxide-carbon monoxide-oxygen

With 5.4 Torr of oxygen added to the mixture of hydrogen peroxide and carbon monoxide, no hydrogen was formed. In the presence of ^{18}O labelled oxygen, ^{18}O was incorporated in the carbon dioxide formed. Although we have carried out some experiments in which the yield of carbon dioxide with time was determined, the most useful information to be obtained in this system was the initial rate of carbon dioxide formation. The results obtained are given in Table I. The rates given are simply those obtained from the yield of carbon dioxide in a time interval during which the initial concentration of any reactant did not change by more than 1.5%. For all of the results reported, the initial pressure of hydrogen peroxide was 0.94 Torr and of oxygen was 5.40 Torr.

Hydrogen peroxide-carbon monoxide-oxygen-isobutane

Mixtures of hydrogen peroxide, oxygen and isobutane yielded no carbon dioxide on irradiation. With carbon monoxide added, carbon dioxide was formed. The results obtained, analogous to those above, are shown in Table II. The initial pressures of hydrogen peroxide and oxygen were the same as for the experiments reported in Table I. The pressure of carbon monoxide was 9.53 Torr and the arc current was 8.0 ma.

Hydrogen peroxide-carbon monoxide-oxygen-propionaldehyde

Irradiation of mixtures of propionaldehyde and oxygen or mixtures of hydrogen peroxide, propionaldehyde, and oxygen yielded carbon dioxide on irradiation. Therefore the method used to obtain rate constants for hydroxyl with hydrogen peroxide and isobutane was not directly applicable. Because the source of carbon dioxide from the aldehyde is not from carbon monoxide, it seemed possible to make a correction by using isotopically labelled O_2

containing ^{18}O. To this time, these experiments have not been successful. However, some quantitative experiments were carried out and the results are shown in Table III. The initial conditions were: hydrogen peroxide, 0.94 Torr; carbon monoxide, 15.6 Torr; arc, 8.0 ma.

DISCUSSION

Mechanism

The minimum number of mechanistic steps necessary to derive rate expressions from the experimental results are

$$H_2O_2 + h\nu(254\ nm) \rightarrow 2OH \qquad (1)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (2)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (3)$$

$$OH + CO \rightarrow CO_2 + H \qquad (4)$$

$$H + H_2O_2 \rightarrow H_2O + OH \qquad (5)$$

$$H + H_2O_2 \rightarrow H_2 + HO_2 \qquad (6)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (7)$$

$$OH + (CH_3)_3CH \rightarrow H_2O + (CH_3)_3C \qquad (8)$$

$$OH + (C_2H_5)CHO \rightarrow H_2O + (C_2H_5)CO \qquad (9)$$

Some water, less than 0.2 Torr, was present in all experiments because hydrogen peroxide was introduced from an aqueous solution. However, the reactions of hydrogen atom and perhydroxyl radical with water need not be included since they are endothermic by 15 and 30 kcal per mole respectively and have rate constants too low to be competitive in the systems studied. It may seem strange that we have not included the reaction

$$HO_2 + CO \rightarrow CO_2 + OH \qquad (10)$$

which has sometimes been tacitly assumed to be fast, presumably because of its large exothermicity of 65 kcal.[4] However, there is no experimental

evidence in our work which indicates it need be invoked, and the following development shows that it has a very low rate constant and may be neglected. The rate constant for the reaction

$$HO_2 + H_2 \rightarrow H_2O_2 + H \qquad (11)$$

is $k_{11} = 1.6 \times 10^{-11} \exp[-24{,}000/RT]$ cm^3 molecule^{-1}sec^{-1}.[5] Baldwin et al.[6] give $k_{10}/k_{11} \cong 10$ at 500°C. The steric factor for reaction (10) is certainly in the range of $1.0\text{-}10^{-6}$ and with this extreme range calculation yields $k_{10} \cong 10^{-28}\text{-}10^{-22}$cm^3 molecule^{-1}sec^{-1} at 298°K. Undoubtedly there are large uncertainties in this calculation, but these are encompassed in the large range.

Calculation of Light Intensity

From eqs. (1), (2), and (3), the only ones applicable to the photolysis of hydrogen peroxide in an inert gas, with the usual steady-state approximation for free radical concentrations the corresponding rate expression is

$$\frac{-d[H_2O_2]}{dt} = 2I_a \qquad (12)$$

The maximum pressure of hydrogen peroxide used in any of our experiments was below 1.0 Torr and the decadic absorption coefficient, ϵ, of hydrogen peroxide at 254 nm is 19.6 l mole^{-1}cm.[7] With these pressures and values of ϵ, terms beyond the first in series expansion of the Lambert-Beer law may be dropped and

$$I_a = I_o \epsilon l [H_2O_2] \qquad (13)$$

or with a fixed illumination geometry

$$I_a = I_o'[H_2O_2] \qquad (14)$$

The corresponding rate expression is then

$$\frac{-d[H_2O_2]}{dt} = 2I_o'[H_2O_2] \qquad (15)$$

which upon integration yields

$$\ln \frac{[H_2O_2]_o}{[H_2O_2]_o - 2[O_2]} = 2I_o't \qquad (16)$$

Thus values of I_o', which are needed in subsequent developments, may be determined from the slopes of the lines in Fig. 1. The values obtained are: line A (1.0 ma), 6.6×10^{-5}; line B (8.0 ma), 8.7×10^{-4}; and line C (15.0 ma), 1.9×10^{-3} sec^{-1}.

Relative rate constants for the reactions of hydrogen atoms with hydrogen peroxide

The results given in Fig. 2 show that oxygen is formed in the irradiation of mixtures of hydrogen peroxide and carbon monoxide. However, in the limit of zero time, oxygen is not present and eq. (7) as a mechanism for the reaction of hydrogen atoms may be ignored. With these conditions a steady state treatment gives

$$\frac{k_5}{k_6} = \left(\frac{d[CO_2]/dt}{d[H_2]/dt}\right)_o^{-1} \qquad (17)$$

From the initial slope of the curves for carbon dioxide and hydrogen formation in Fig. 2, the value obtained is $k_5/k_6 = 3.0 \pm 1.0$ at 298°K.

The only other value given for this ratio is that of Baldwin et.al.,[6] $k_5/k_6 \cong 6.2$ at 713°K. From this value and ours at 298°K, the calculated difference in activation energies is $E_5 - E_6 \cong 700$ cal. Individual rate constants, k_5 and k_6, are known only with a very large degree of uncertainty,[5] and therefore it is not possible to make a meaningful comparison of our ratio with one calculated from rate constants.

Rate constant for the reaction of hydroxyl with hydrogen peroxide

Since irradiated mixtures of hydrogen peroxide, carbon monoxide, and oxygen yielded no hydrogen, the only reaction of hydrogen atom which need be considered is reaction (7). The derived rate expression is

$$\frac{2I_o'}{(d[CO_2]/dt)_o} = \frac{1}{[CO]_o}\,\frac{k_2}{k_4} + \frac{1}{[H_2O_2]_o} \qquad (18)$$

The data of Table I plotted in conformance with this expression are shown in Fig. 3. The straight line was constructed from a least squares analysis using all the experimental values over the 29 fold intensity range. The slope yields

$$k_2/k_4 = 8.13 \pm 0.56$$

Although this is a relative rate ratio, we believe it yields a reliable value of k_2 because k_4 is accurately known. Recent work at about room temperature by three different techniques[8] yields values of k_4, three of which are in excellent agreement and one of which is in reasonable agreement. This data has been critically evaluated,[9] and the value recommended is $1.5 \pm 0.3 \times 10^{-13}$ cm^{3}molecule^{-1}sec^{-1} at 298°K. (A recalculation[10] of one of the values used[8(c)] does not change this recommended value). From this value of k_4 the value of k_2 obtained in this work is $k_2 = 1.2 \pm 0.3 \times 10^{-12}$ cm^{3}molecule^{-1}sec^{-1} at 298°K. The only other experimental determination of this rate constant below 700°K is that of Greiner[11] who reported $k_2 = 9.3 \times 10^{-13}$ cm^{3}molecule^{-1}sec^{-1} obtained by a kinetic spectroscopy study of the flash photolysis of hydrogen peroxide. This value is in excellent agreement with our result.

Rate Constant for the reaction of hydroxyl with isobutane

An objective of this study was to evaluate the feasibility of obtaining rate constants for hydroxyl radical reactions by competitive kinetics based solely on analysis of carbon dioxide. Isobutane seemed ideally suited for such a study. It is transparent at 254 nm and therefore would not affect the intensity of light absorbed by hydrogen

peroxide. As it contains only primary and tertiary hydrogen atoms, it would be expected that abstraction by hydroxyl would occur predominantly, over 83 percent,[12] from the tertiary hydrogen atom. Also it was found in our experiments that carbon dioxide was not formed on irradiation of mixtures containing hydrogen peroxide, oxygen, and isobutane.

With enough added oxygen so that the only reaction of hydrogen atom is reaction (7) and with the inclusion of reaction (8), the rate expression is

$$\frac{2I_0'}{(d[CO_2]/dt)_0} = \frac{k_2}{k_4[CO]_0} + \frac{1}{[H_2O_2]_0} + \frac{k_8[RH]_0}{k_4[CO]_0[H_2O_2]_0} \qquad (19)$$

With I_0', $[CO]_0$, and $[H_2O_2]_0$ held constant, the independent variable is $[RH]_0$. The data of Table II plotted in conformance with this expression are shown in Fig. 4. The straight line was constructed from a least squares analysis and calculation from the slope yields $k_8/k_4 = 23.3 \pm 0.7$ from which $k_8 = 3.5 \pm 0.8 \times 10^{-12}$ cm^{3}molecule^{-1}sec^{-1}. This value is in reasonable agreement with the only one for comparison which is again that of Greiner, $k_8 = 2.3 \pm 0.2 \times 10^{-12}$ cm^3 molecule^{-1}sec^{-1} determined by flash photolysis-kinetic spectroscopy.[12]

Rate constant for the reaction of hydroxyl with propionaldehyde

For the reasons given earlier the preliminary data obtained with propionaldehyde was from experiments without added oxygen. If reaction (7) is therefore excluded, the rate expression becomes

$$\frac{2I_0'}{(d[CO_2]/dt)_0} = \frac{k_2}{k_4[CO]_0} + \frac{k_9[(C_2H_5)CHO]_0}{k_4[CO]_0[H_2O_2]_0} \qquad (10)$$

From this experssion, the data of Table III yield $k_9 = 3.8 \pm 1.5 \times 10^{-12}$ cm^3 molecule^{-1}sec^{-1}. Experiments with this system are being continued with the hope that the large error limits may be reduced and that an experimental method applicable to other aldehydes may be successfully developed.

REFERENCES

1. D. H. Volman, J. Chem. Phys., 1949, 17, 947.

2. D. H. Volman, Advan. Photochem., 1963, 1, 43.

3. H. Melville and B. G. Gowenlock, Experimental Methods in Gas Reactions, 2nd Ed., Macmillan, London, 1964, p. 165.

4. S. W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960, p. 461.

5. D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems, School of Chemistry, The University, Leeds, 1969, No. 3.

6. R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, Tenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1965, p. 423.

7. R. B. Holt, C. K. McLane, and O. Oldenberg, J. Chem. Phys., 1948, 16, 225.

8. (a) G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys., 1966, 44, 2877.

   (b) J. T. Herron, J. Chem. Phys., 1966, 45, 1854.

   (c) N. R. Greiner, J. Chem. Phys., 1967, 46, 2795.

   (d) W. E. Wilson and J. T. O'Donovan, J. Chem. Phys., 1967, 47, 5455.

9. Ref. 5, 1968, No. 1.

10. N. R. Greiner, J. Chem. Phys., 1969, 51, 5049.

11. N. R. Greiner, J. Phys. Chem., 1968, 72, 406.

12. N. R. Greiner, J. Chem. Phys., 1970, 53, 1070.

TABLE I

Initial Rate of CO_2 Formation in the H_2O_2-CO-O_2 System

Arc current ma	CO Torr	$(d[CO_2]/dt)_o$ (Torr min^{-1})x10^2
1.0	2.83	0.17
	4.94	0.29
	4.97	0.30
	4.98	0.25
	14.25	0.42
	19.96	0.37
	31.90	0.49
8.0	3.18	3.0
	6.32	4.3
	7.91	5.5
	9.52	5.1
	11.86	6.3
	12.66	5.4
	12.69	5.8
	14.23	6.3
	15.88	6.0
	19.04	6.3
	19.16	6.4
	20.74	7.8
	22.36	6.8
15.0	4.94	8.8
	19.98	13.8

TABLE II

Initial Rate of CO_2 Formation in the H_2O_2-CO-O_2-$(CH_3)_3CH$ System

$(CH_3)_3CH$ Torr	$(d[CO_2]/dt)_o$ (Torr min^{-1})x10^4
0	7.50
0.128	7.00
0.249	5.17
0.445	5.17
0.760	3.67
0.999	3.50
1.25	3.00
1.56	3.00
1.96	2.50
2.54	2.00
3.15	1.67
4.69	1.17

TABLE III

Initial Rate of CO_2 Formation in the H_2O_2-CO-$(C_2H_5)CHO$ System

$(C_2H_5)CHO$ Torr	$(d[CO_2]/dt)_o$ Torr min^{-1}
0.0010	0.20
0.030	0.19
0.057	0.18
0.12	0.15
0.16	0.16
0.23	0.13

LEGENDS FOR FIGURES

Fig. 1. Decomposition of H_2O_2 irradiated at 254 nm and 25°C. arc current: A, 1.0; B, 8.0; C, 15.0 ma.

Fig. 2. Product yields for mixtures of H_2O_2 and CO irradiated at 254 nm and 25°C.

Fig. 3. Photochemical reaction in mixtures of H_2O_2, CO, and O_2 at 254 nm and 25°C.
I_o': ○, 6.6×10^{-5}; □, 8.7×10^{-4}; +, 1.9×10^{-3} sec^{-1}.

Fig. 4. Photochemical reaction in mixtures of H_2O_2, CO, O_2, and $(CH_3)_3CH$ at 254 nm and 25°C. $I_o' = 9.1\times10^{-4}$ sec^{-1}.
Initial pressures: H_2O_2, 0.94; CO, 9.53; and O_2, 5.45 Torr.

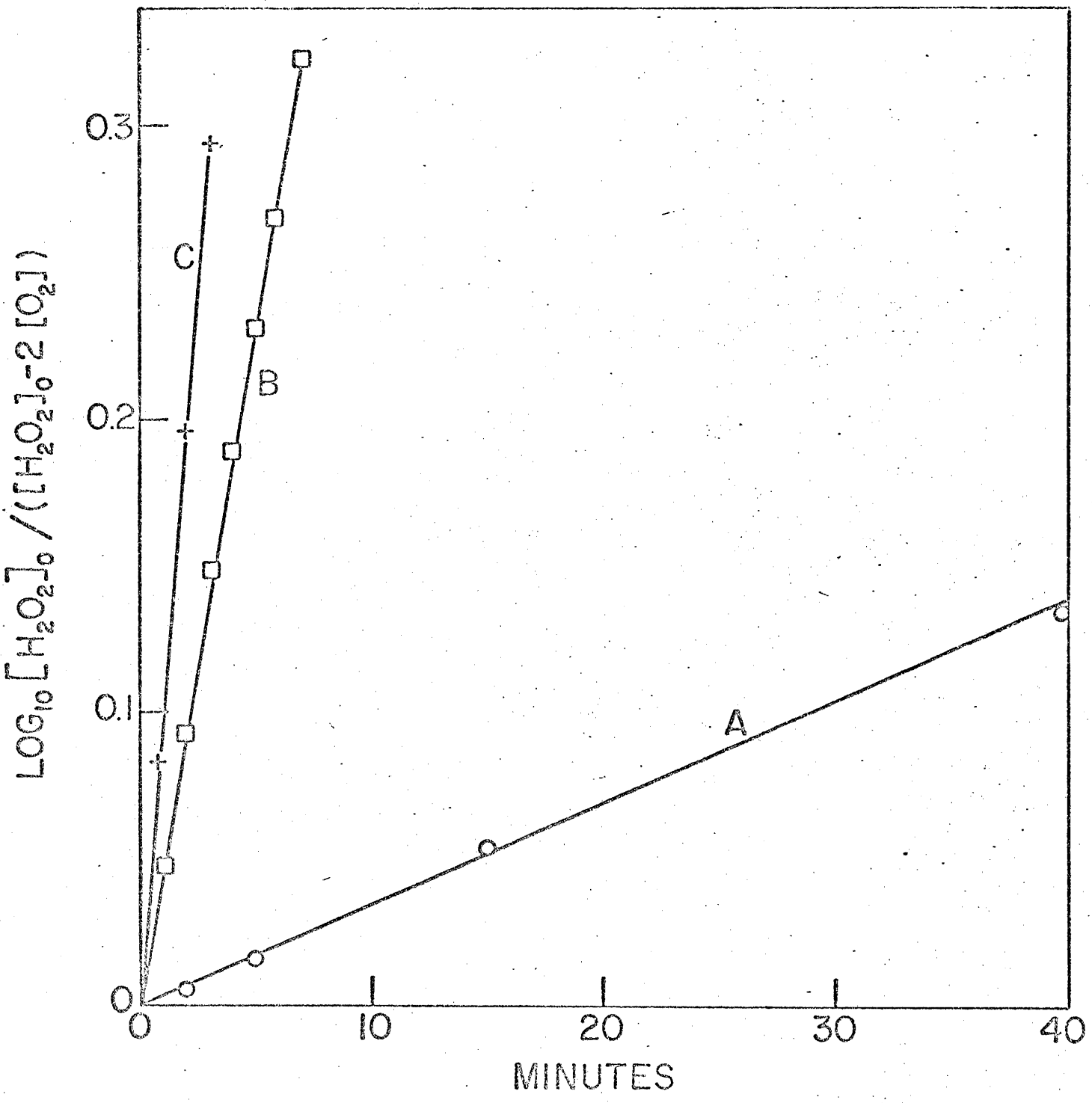

Fig. 1

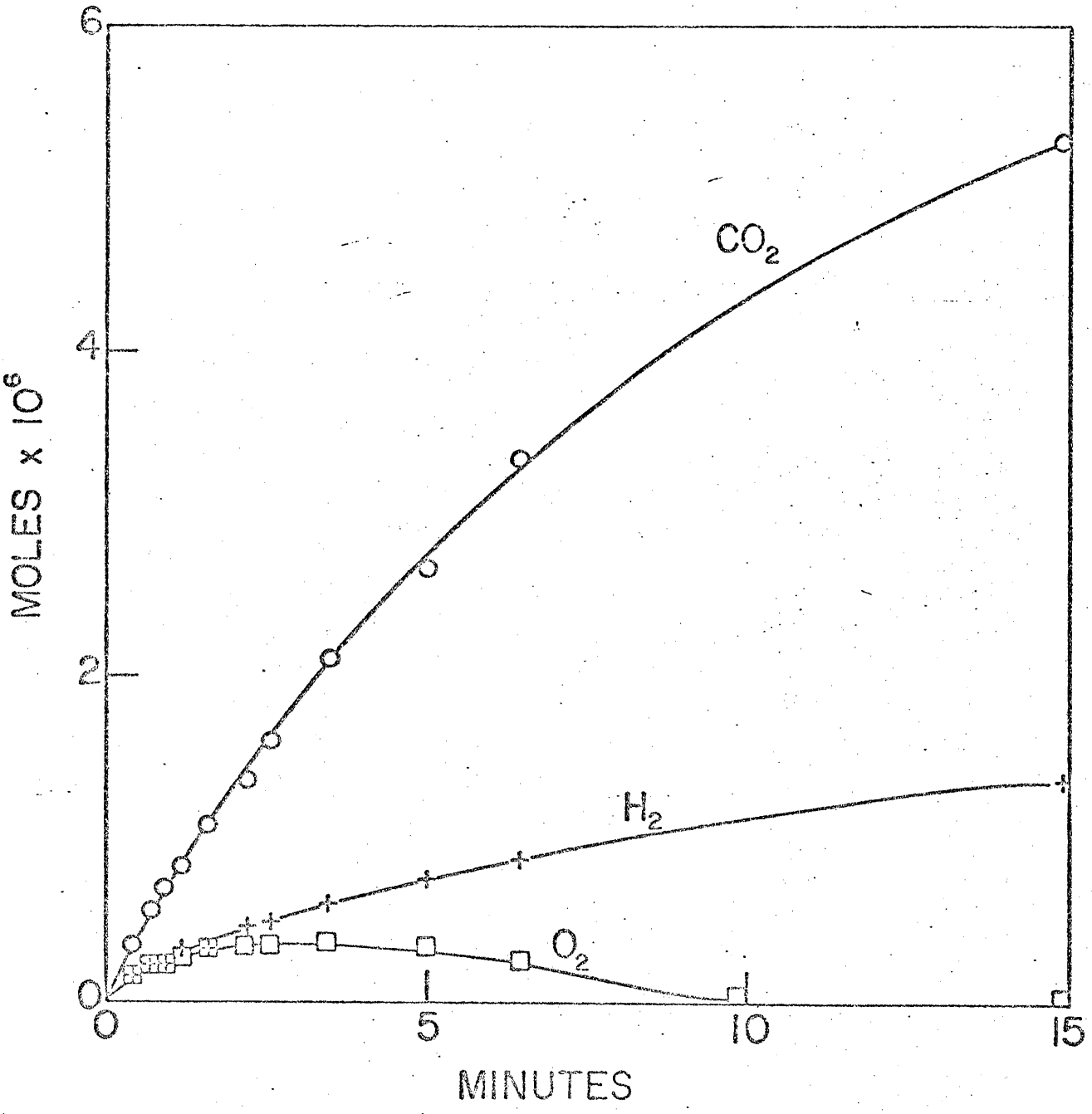

Fig. 2

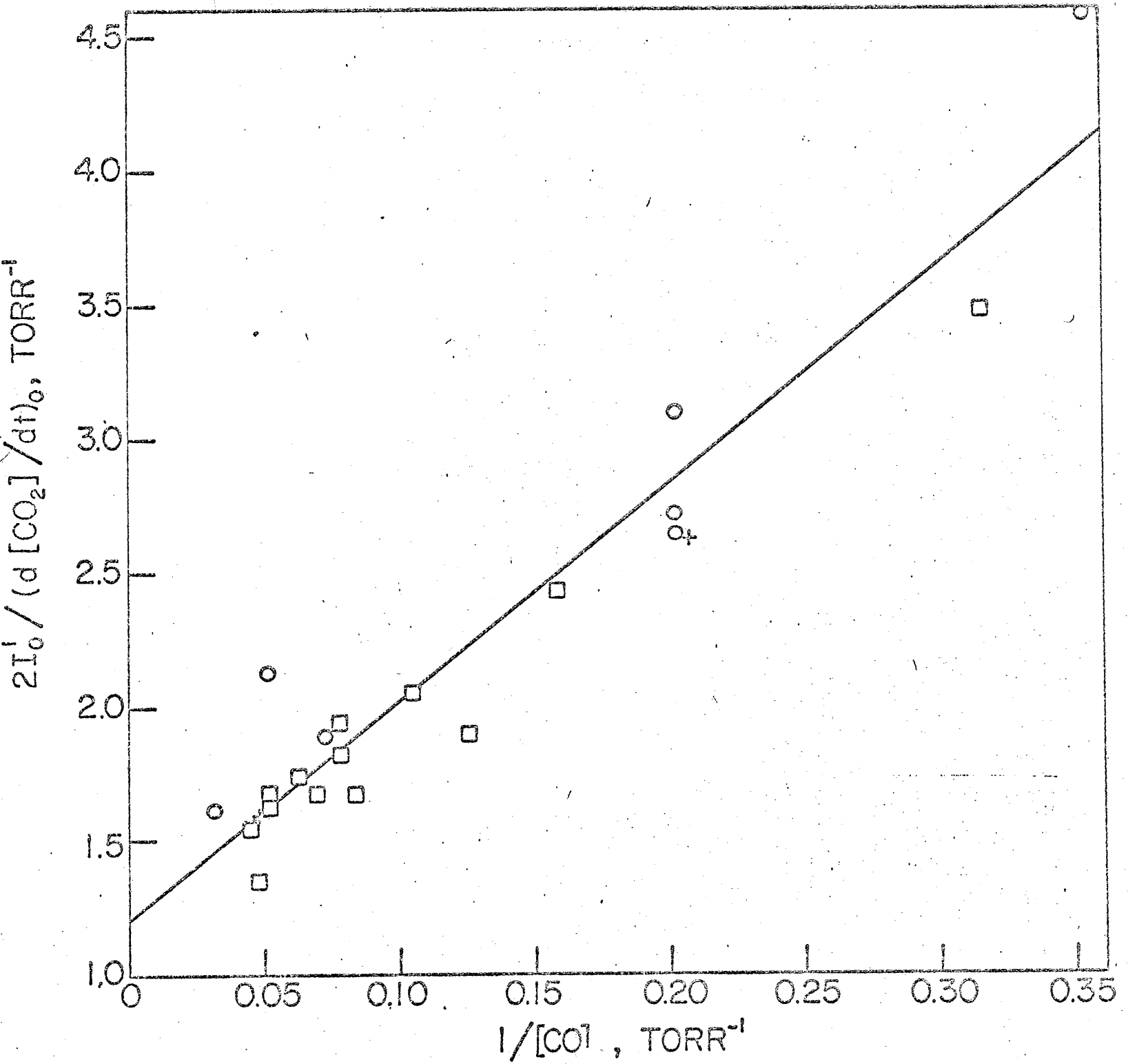
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
$2I_o'/(d[CO_2]/dt)_o$, TORR^{-1}
$1/[CO]$, TORR^{-1}

Fig. 3

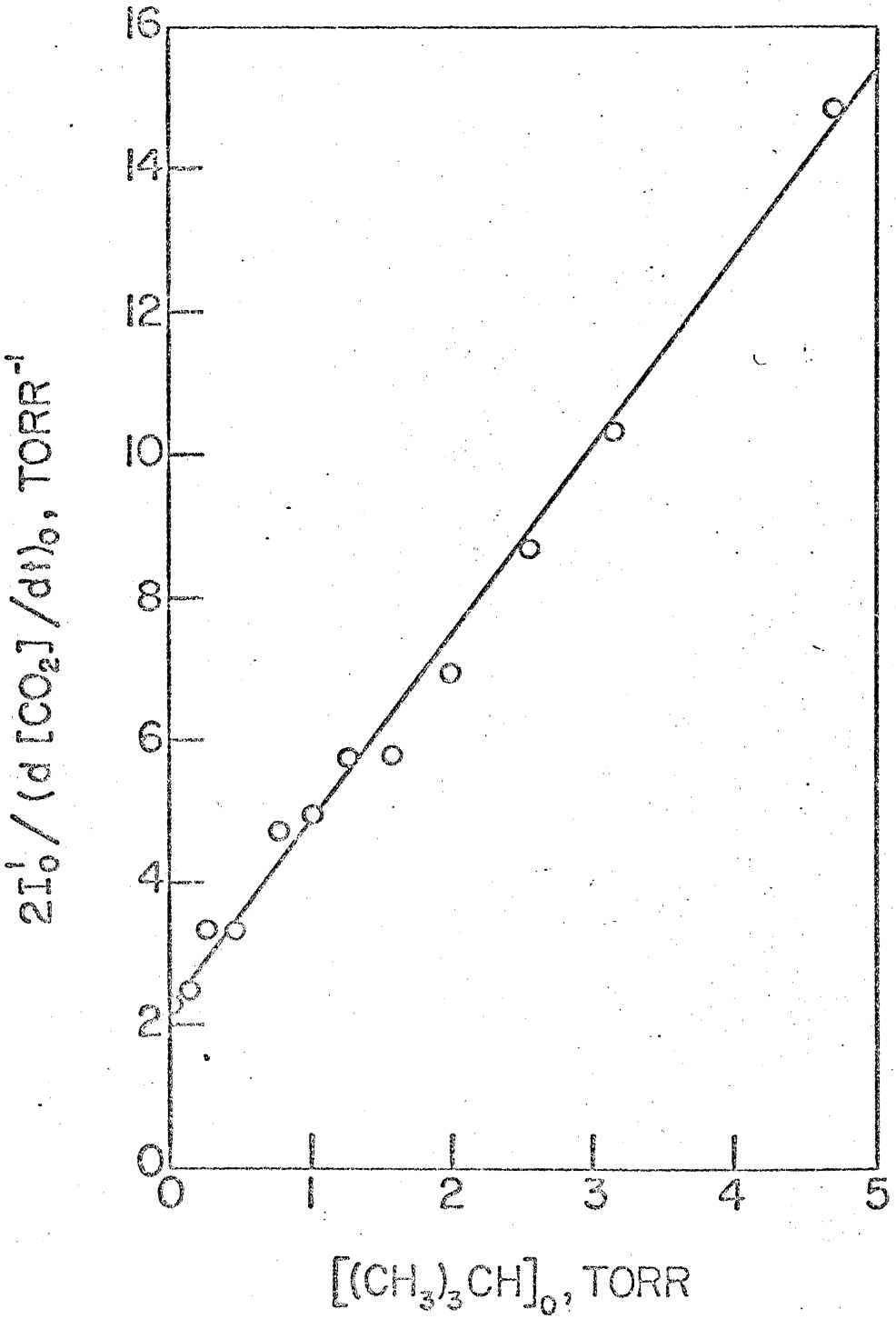

Fig. 4